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Understanding the origins of N_2O decomposition activity in Mn(Fe)CoAlO_x hydrotalcite derived mixed metal oxides

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ABSTRACT

The catalytic decomposition of N_2O was studied over a series of calcined Mn(Fe)CoAl hydrotalcite-like compounds. The precursors were prepared by coprecipitation and characterized by XRD and TGA. The mixed metal oxides derived after calcination at 600 °C were characterized by XRD, N_2 adsorption, H_2-TPR and XPS. Moreover, in situ XAFS measurements over selected mixed metal oxides were performed. Such investigations under relevant reaction conditions are rare, while a comprehensive understanding of the involved active species may facilitate a knowledge-based catalyst optimization. The activity of the CoAlO_x (Co/Al = 3/1, mol.%) catalyst varied depending on the loading of Mn or Fe (0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%). In the investigated series, $Mn_{0.1725}Co_3Al_1O_x$ reached the highest activity with T_{50} of about 305 and 376 °C under N_2O/N_2 and N_2O,NO,O_2/N_2 feed, respectively. In situ X-ray absorption experiments over $Mn_{0.1725}Co_3Al_1O_x$ suggested that $Mn_xCo_yO_4$ spinels undergo reduction to CoO and MnO upon heating up to 600 °C in He. Under N_2O/He conditions, initial reoxidation of cobalt species began at 350 °C. The lower activity obtained for $Fe_{0.1725}Co_3Al_1O_x$ is explained by the fact that the majority of Fe was not incorporated into the Co_3O_4 structure but instead formed less reactive iron oxide clusters.

1. Introduction

The catalytic decomposition of N_2O (deN_2O) can be considered as one of the best available technologies for N_2O abatement from nitric acid production, which is one of its major industrial sources. A broad collection of catalysts has been investigated at temperatures below 450–500 °C [1]. As implied by the published results, hydrotalcite derived mixed metal oxides present high activity for deN_2O even in the presence of H_2O, O_2, SO_2 and/or NO_x. The hydrotalcite-like compounds with a general formula of $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} – bi- and trivalent metal cations, respectively, A^{n-} – an interlayer anion and x – $M^{3+}/(M^{3+}+M^{2+})$ with a value between 0.17–0.50 [2,3], serve as excellent precursors for the preparation of catalysts of the desired chemical and phase composition for deN_2O. Thermal decomposition of hydrotalcite-like compounds at middle temperatures (≤600 °C) results in the formation of relatively high surface area mixed metal oxides with a high dispersion of introduced transition oxide metal species [4–6]. Recently, Jabłońska and Palkovits [1,7] reviewed hydrotalcite derived mixed metal oxides in deN_2O and concluded that the activity of the mixed metal oxides varied depending on the type and loading of the catalytically active metal, its oxidation state as well as dispersion and aggregation state, etc. The research of hydrotalcite derived mixed metal oxides focusses mainly on cobalt-based materials: CoAlO_x (e.g. [8,9]), Co(Mg)Mn(Al)O_x (e.g. [10–12]), CoMgAlO_x or CoCuMgAlO_x (e.g. [13]), etc. Kannan et al. [14–16] and furthermore Pérez-Ramírez et al. [8] found Co/Al with 3/1 M ratio as optimal hydrotalcite derived catalyst dedicated to deN_2O among catalysts varied between Co/Al = 3-1/1, mol.%. $Co_3Al_1O_x$ reached 84% (WHSV = 60 L (h g)$^{-1}$ [15]) to 100% (WHSV = 120 L (h g)$^{-1}$ [8]) conversion at 450 °C. Kannan et al. [15,16] reported that the activity of

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$CoAlO_x$ mixed metal oxides correlated with the Co/Al bulk composition, but, an even better correlation in the activity was obtained with the Co^{2+} (generated by surface reduction and reconstruction) of mixed metal oxides, as determined by XPS. Obalová et al. [10,11,17] investigated numerous combinations of $Co(Mg)Mn(Al)O_x$ and found $Co_4Mn_1Al_1O_x$ as optimum catalyst for deN_2O (82–97% conversion at 450 °C, WHSV = 60 L (h g)$^{-1}$). The authors reported an optimum surface amount of Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+} molar ratios at 1.13 and 2.27 by XPS. Moreover, as determined from H_2-TPR, $Co_4Mn_1Al_1O_x$ possessed an optimum number of components reducible in the temperatures of the maximum conversion of N_2O (between 350–450 °C) [11]. We note that to date there are no studies on hydrotalcite derived catalysts under reaction conditions available and as such insight into the active form of the catalyst is currently absent. Such information however, often provides a better understanding of what makes for a good or poor catalyst. Our present investigation focused on identifying the exact nature and behaviour of metal species in $Mn(Fe)CoAlO_x$ mixed metal oxides applied to deN_2O using in situ XAFS supported by ex situ characterisation of precursors and/or mixed metal oxides using XRD, TG, N_2 adsorption and H_2-TPR, in order to explore additional structure-activity correlations.

2. Experimental

2.1. Catalyst preparation

A series of $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds was prepared by coprecipitation. An aqueous solution containing appropriate amounts of following metal nitrates: $Co(NO_3)_2{\cdot}6H_2O$ (Roth), $Al(NO_3)_3{\cdot}9H_2O$ (Sigma), $Mn(NO_3)_2{\cdot}4H_2O$ (Roth), $Fe(NO_3)_3{\cdot}9\,H_2O$ (Roth) and 1 M NaOH (Chemsolute) was dropped simultaneously into a vigorously stirred aqueous solution containing a slight over-stoichiometric excess of Na_2CO_3 (Sigma) at 60 °C. The pH of the reaction mixture was maintained constant at 10.0 ± 0.2 throughout the whole synthesis by NaOH addition. The obtained suspension was aged at 60 °C for another 0.5 h after complete coprecipitation. The solid was filtered, washed carefully with distilled water and dried at room temperature. Finally, the prepared hydrotalcite-like compounds were crushed and calcined at 600 °C for 6 h with a heating ramp of 10 K min^{-1} and in static air. The hydrotalcite derived mixed metal oxides were kept in a desiccator in order to avoid the reconstruction of the hydroxide-like structure. For catalytic experiments, a fraction of particle size in the range of 0.250–0.500 mm was used.

2.2. Catalyst characterization

The X-Ray diffraction (XRD) measurements of the all as-synthesized hydrotalcite-like compounds and mixed metal oxides formed by their thermal decomposition was performed on a Siemens D5000 XRD diffractometer using Cu-Kα radiation (λ = 1.54056 Å, 45 kV, 40 mA).

The difference thermogravimetric analyses (DTG) of the hydrotalcite-like compounds (~20 mg) were carried out using a Netzsch STA 409C/CD operated under a flow of air (10 cm^3 min^{-1}) in the temperature range of 30–1000 °C with a linear heating rate of 5 K min^{-1}.

The specific surface area (S_{BET}) of the mixed metal oxides was determined by low-temperature (−196 °C) N_2 sorption using a Quantachrome Quadrasorb SI. Prior to nitrogen adsorption the samples were outgassed at 250 °C for 12 h using a Quantachrome Flovac degasser. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) multiple point method in the p/p_0 range from 0.05 to 0.3.

The chemical analysis of mixed metal oxides was determined by ICP-MS using an Agilent Technologies 8800 Triple Quad spectrometer. Prior to measurement, the sample (50 mg) was dissolved in 6 cm^3 mixture of concentrated acids ($HCl:HNO_3$, 1:1), and afterwards the resulting mixture was diluted with 64 cm^3 deionized water before warming up to 40 °C for 24 h.

The redox properties of the selected mixed metal oxides were studied by the temperature-programmed reduction (H_2-TPR) using Quantachrome ChemBET Pulsar TPR/TPD. H_2-TPR runs for the samples (30 mg) were carried out starting from room temperature to 1000 °C with a linear heating rate of 10 K min^{-1} and in a flow (25 cm^3 min^{-1}) of 5.0 vol.% H_2/Ar. Water vapour was removed from effluent gas by means of a cold trap placed in an ice-water bath. The H_2 consumption was detected and recorded by TCD detector.

The X-ray photoelectron spectra (XPS) of selected mixed metal oxides were measured on a VSW spectrometer equipped with a hemispherical analyzer. The photoelectron spectra were measured using a magnesium Mg K_α source (E = 1253.6 eV). The base pressure in the analysis chamber during the measurements was $3{\cdot}10^{-6}$ Pa and the spectra were calibrated on a main carbon C 1s peak at 284.6 eV. The composition and chemical surrounding of the sample surface were investigated based on the areas and binding energies of Co 2p, Mn 2p, Fe 2p, Al 2p, O 1 s and C 1 s photoelectron peaks. Mathematical analyses of the XPS spectra were carried out using the XPSpeak 4.1 computer software (RWM. Kwok, The Chinese University of Hong Kong).

The X-ray absorption spectra (XAS) of selected samples were collected in situ using the quartz capillary flow reactor cells and gas delivery systems available on the beamline, on station B18 at the Diamond Light Source synchrotron facility. The measurements were carried out using a Si(111) monochromator at the Co K-edge, Mn K-edge or Fe K-edge with the respective Co, Mn or Fe monometallic foils (10 μm) used as an energy calibrant for the monochromator. The catalyst diluted with SiO_2 (1:5) was sieved into 0.200–0.250 mm and placed into the reactor. Prior to the reaction the catalyst was outgassed at 600 °C for 1 h in a flow of pure He (10 cm^3 min^{-1}), and subsequently cooled down to 100 °C. The reactant concentrations at the reactor inlet composed of $[N_2O]$ = 0.1 vol.% and He balance (10 cm^3 min^{-1}). The temperature was raised in steps of 50–100 °C up to 600 °C. Each temperature was held for 30 min for spectra acquisition. Finally, the sample was cooled down to room temperature under pure He. X-ray absorption spectra at

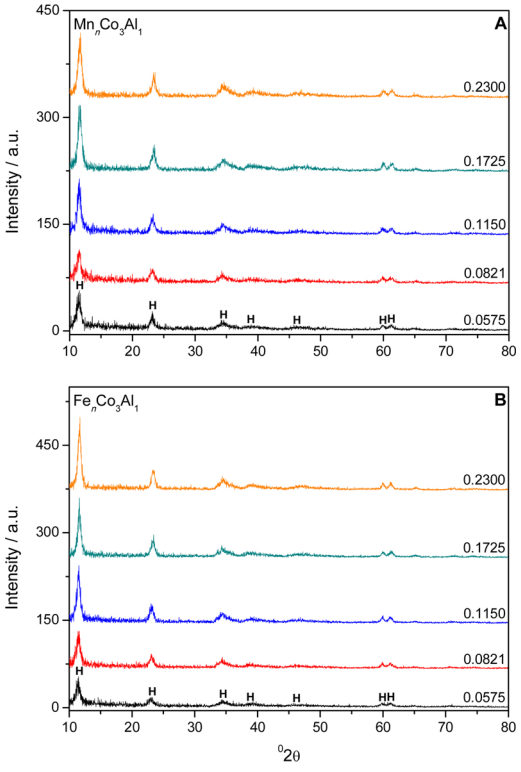

Fig. 1. X-ray diffraction patterns of $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds; H – hydrotalcite-like phase.

Table 1
Lattice parameters of (Mn,Fe)CoAl hydrotalcite-like compounds and corresponding mixed metal oxides.

Hydrotalcite-like compounds	Cell parameter *a*/nm	Cell parameter *c*/nm	Crystallite size Da/nm	Crystallite size Dc/nm	Mixed metal oxides	Cell parameter *a*/nm	Crystallite size Da/nm
Co_3Al_1	0.3079	2.2956	29	20	$Co_3Al_1O_x$	27	0.8093
$Mn_{0.0575}Co_3Al_1$	0.3085	2.3065	33	22	$Mn_{0.0575}Co_3Al_1O_x$	32	0.8076
$Mn_{0.0821}Co_3Al_1$	0.3086	2.3060	34	21	$Mn_{0.0821}Co_3Al_1O_x$	32	0.8083
$Mn_{0.1150}Co_3Al_1$	0.3085	2.3006	25	24	$Mn_{0.1150}Co_3Al_1O_x$	27	0.8099
$Mn_{0.1725}Co_3Al_1$	0.3080	2.2800	33	24	$Mn_{0.1725}Co_3Al_1O_x$	26	0.8079
$Mn_{0.2300}Co_3Al_1$	0.3078	0.2790	27	24	$Mn_{0.2300}Co_3Al_1O_x$	26	0.8099
$Fe_{0.0575}Co_3Al_1$	0.3085	2.3215	22	22	$Fe_{0.0575}Co_3Al_1O_x$	30	0.8073
$Fe_{0.0821}Co_3Al_1$	0.3086	2.3100	39	26	$Fe_{0.0821}Co_3Al_1O_x$	33	0.8076
$Fe_{0.1150}Co_3Al_1$	0.3085	2.3065	39	28	$Fe_{0.1150}Co_3Al_1O_x$	33	0.8093
$Fe_{0.1725}Co_3Al_1$	0.3081	2.2839	34	28	$Fe_{0.1725}Co_3Al_1O_x$	30	0.8083
$Fe_{0.2300}Co_3Al_1$	0.3081	2.2790	42	30	$Fe_{0.2300}Co_3Al_1O_x$	31	0.8096

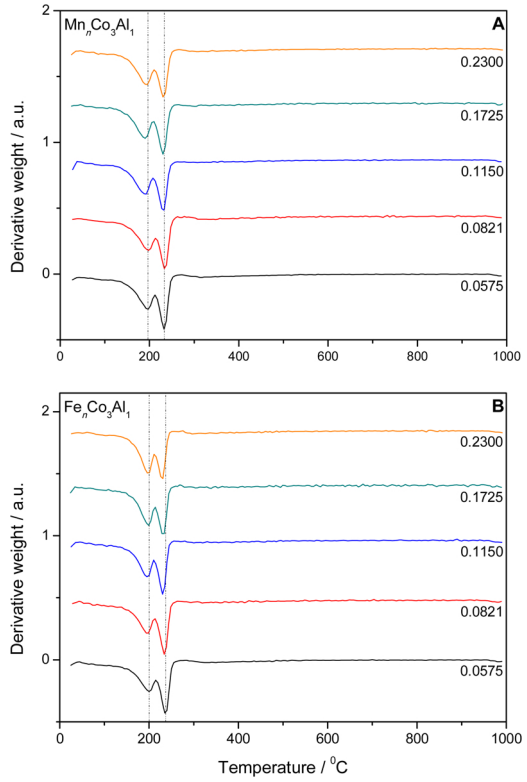

Fig. 2. DTG profiles of $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds; experimental conditions: mass of sample = 20 mg, flow of synthetic air = 10 $cm^3\,min^{-1}$, liner heating rate of 5 K min^{-1}.

appropriate K-edges were collected in fluorescence mode for 240 s for Co, Fe or Mn K-edges. At least three spectra for each sample were taken (and averaged) at room temperature, appropriate temperatures and after reaction at room temperature. CoO, Co_3O_4, FeO, Fe_2O_3, MnO_2 references were measured only at room temperature. The data were analysed using the Demeter software package [18,19]); the edge position was determined as the first maximum – after the pre-edge peak – of the derivative of the XANES spectra.

2.3. Catalytic tests

The catalytic activity and selectivity of the mixed metal oxides was evaluated in the N_2O decomposition. The catalytic experiments were carried out under atmospheric pressure in a fixed-bed flow microreactor of 6 mm internal diameter. Prior to the reaction the catalyst (350 mg) was outgassed at 600 °C for 1 h in a flow of pure N_2 (100 $cm^3\,min^{-1}$). The reactant concentrations at the reactor inlet composed of: (i) $[N_2O]$ = 0.1 vol.%, N_2 balance, (ii) $[N_2O]$ = 0.1 vol.%, [NO] = 0.03 vol.%, $[O_2]$ = 4.5 vol.%, N_2 balance (100 $cm^3\,min^{-1}$; WHSV = 17 L (h g)$^{-1}$, and were analyzed by infrared spectroscopy using a Perkin Elmer Spectrum Two equipped with a Pike 5 m heated gas cell. The temperature was raised in steps of 50 °C starting from 100 up to 600 °C. Each temperature was set constant for 0.5 h.

For selected material, additional tests were performed in the presence of water vapour. Such catalytic experiments were carried out under atmospheric pressure in a fixed-bed flow microreactor of 9 mm internal diameter. Prior to the reaction, the catalyst (70–150 mg) was activated at 580 °C for 0.5 h in a flow of pure He (75 $cm^3\,min^{-1}$). After reactor cooled down, the following composition was applied: $[N_2O]$ = 0.1 vol.%, ($[H_2O]$ = 3.5 vol.%), He balance (75 $cm^3\,min^{-1}$; WHSV = 30–64 L (h g)$^{-1}$), and were analyzed by a Pfeiffer Omnistar quadrupole mass spectrometer equipped with Channeltron and Faraday detectors (0–200 amu). Water vapour was added by means of a saturator whose temperature was controlled by a thermostat.

The conversion of N_2O ($X(N_2O)$) was estimated according to $X(N_2O) = ([c(N_2O)_{in} - c(N_2O)_{out}]/c(N_2O)_{in})$ x 100%, where: $c(N_2O)_{in}$ and $c(N_2O)_{out}$ – concentration of N_2O in the inlet gas, and concentration of N_2O in the outlet gas.

Table 2
Total mass loss of (Mn,Fe)CoAl hydrotalcite-like compounds, specific surface area (S_{BET}), sodium residuals of mixed metal oxides, and T_{50} of mixed metal oxides in N_2O/N_2, N_2O,NO,O_2/N_2* and N_2O,H_2O/He** gas mixtures.

Hydrotalcite-like compounds	Total mass loss/%	Mixed metal oxides	S_{BET}/m^2g^{-1}	Na/wt.%	T_{50}/°C
Co_3Al_1	32.62	$Co_3Al_1O_x$	82	1.4	352[a] *409[a] **549[b]
$Mn_{0.0575}Co_3Al_1$	31.90	$Mn_{0.0575}Co_3Al_1O_x$	59	0.7	317[a]
$Mn_{0.0821}Co_3Al_1$	31.54	$Mn_{0.0821}Co_3Al_1O_x$	57	1.3	332[a]
$Mn_{0.1150}Co_3Al_1$	30.53	$Mn_{0.1150}Co_3Al_1O_x$	61	1.0	320[a]
$Mn_{0.1725}Co_3Al_1$	30.89	$Mn_{0.1725}Co_3Al_1O_x$	76	2.3	305[a] *376[a] **528[b]
$Mn_{0.2300}Co_3Al_1$	31.03	$Mn_{0.2300}Co_3Al_1O_x$	65	0.8	316[a]
$Fe_{0.0575}Co_3Al_1$	31.43	$Fe_{0.0575}Co_3Al_1O_x$	56	0.8	356[a]
$Fe_{0.0821}Co_3Al_1$	31.34	$Fe_{0.0821}Co_3Al_1O_x$	53	0.8	325[a]
$Fe_{0.1150}Co_3Al_1$	31.10	$Fe_{0.1150}Co_3Al_1O_x$	54	1.6	333[a]
$Fe_{0.1725}Co_3Al_1$	30.27	$Fe_{0.1725}Co_3Al_1O_x$	54	0.9	327[a] *380[a] **549[b]
$Fe_{0.2300}Co_3Al_1$	31.00	$Fe_{0.2300}Co_3Al_1O_x$	50	0.9	355[a]

[a] 350 mg of catalyst, 100 $cm^3\,min^{-1}$ total flow.
[b] 70 mg of catalyst, 75 $cm^3\,min^{-1}$ total flow.

3. Results and discussion

Firstly, the structure of our precursors has been controlled to ensure that mixed metal oxide catalysts were issued from a material having the

same structure. Fig. 1 presents the XRD patterns of $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds, exhibiting rhombohedral symmetry (space group R3m, $3R_1$ polytype) [20] with sharp and symmetrical reflections (0 0 3), (0 0 6), (1 1 0) and (1 1 3), and broad and asymmetrical reflections (0 1 2), (0 1 5) and (0 1 8). The intensity of the reflection corresponding to the hydrotalcite-like phase were very weak for samples with 0.0575 mol.% of Mn or Fe. However, the intensity of such phases increased with increasing loading of both transition metals. Table 1 summarizes the unit cell parameters of the hydrotalcite-like compounds and their derivatives. The cell parameters were calculated using the position of (1 0 1) reflection: $a = 2(d_{1\,1\,0})$ and positions of basal reflections: $c = [3(d_{0\,0\,3}) + 6(d_{0\,0\,6})]/2$. The lattice paramater a depends on the size of the cation in the brucite-like layers, while the parameter c refers to the interlayer thickness. The a value for $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds varied only slightly with increasing Mn or Fe content and were close to that obtained for Co_3Al_1. The a value depends mainly on the ionic radii of the cations in octahedral coordination (0.070 nm Co^{2+}, 0.070 nm Mn^{2+} and 0.070 nm Fe^{3+} [21], as cations of metal precursors). The c value of about 2.3 nm stays characteristic for hydrotalcite-like compounds containing carbonates located in the interlayer space [2]. The interlayer distances increased upon decreasing electronegativity of the cations: Co (1.70) > Fe (1.64) > Mn (1.60) > Al (1.47) (according to Allred-Rochow scale) [22]. The crystal size was calculated from the Scherrer equation $D = 0.89 \cdot \lambda/\beta \cdot \theta$, where D is the crystallite size, λ is the X-ray wavelength, β is the line broadening and θ is the Bragg angle. The Fe-containing materials revealed overall higher crystal size (with the exception of $Fe_{0.0575}Co_3Al_1$) than the corresponding $MnCo_3Al_1$ compounds.

Fig. 2 presents the DTG profiles of $Mn(Fe)_nCo_3Al_1$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) hydrotalcite-like compounds, while Table 2 gathers total mass loss of these materials. DTG profiles provided an additional proof of the presence of the hydrotalcite-like structure. The thermal decomposition of Mn(Fe)-Co-Al precursors proceeded in two main stages with total mass losses of about 30–33%. The first DTG minimum centered at about 190–200 °C corresponded to the removal of interlayer and weakly adsorbed water without collapse of the structure. The second peak located at about 230–235 °C appeared due to the dehydroxylation of the brucite-like layers and thermal decomposition of interlayer carbonates and nitrates (e.g. [5,6,20]). The temperatures and peak intensities did not change significantly among studied precursors, possibly due to small differences in the Mn or Fe loading as well as similar size of Mn^{2+} and Fe^{3+} (as cations of metal precursors) in octahedral coordination of 0.070 nm [21].

Fig. 3 shows the XRD patterns of calcined Mn(Fe)CoAl hydrotalcite-like compounds. The hydrotalcite-like structure was completely destroyed upon heating at 600 °C resulting in the formation of a spinel phase with a range of possible composition, namely $Co_3O_4/CoAl_2O_4/Co_2AlO_4$ (with Bragg reflections located at 2θ at 19, 31, 37, 39, 45, 56, 59, 65, 77°, e.g. [8,16]), exhibiting cubic symmetry (space group Fd3m) [23]. The lattice parameter a in the range of 0.8073-0.8099 nm was close to Co_3O_4 (a = 0.8084 nm). Mn- or Fe- containing materials did not reveal any diffraction characteristic of such transition metal oxides in the XRD patterns, which confirmed the absence of bigger crystallites. Crystal sizes of 26–33 nm were calculated from (3 1 1) brag reflection in the XRD patterns using the Scherrer equation.

Table 2 lists the specific surface area (S_{BET}) of the (Mn,Fe)$CoAlO_x$ mixed metal oxides. S_{BET} for $Co_3Al_1O_x$ of 82 $m^2\,g^{-1}$, significantly decreased after introduction of Mn or Fe within its structure. A similar trend was observed for both series, i.e. decrease for materials with 0.0821 mol.% then increase up to 0.1725 mol.% and finally a drop in S_{BET} for materials with the highest loading of transition metal (0.2300 mol.%). However, slightly higher values for S_{BET} were reached over Mn-containing mixed metal oxides. Chemical analysis identified by ICP-MS evidenced sodium residual from preparation procedure up to 2.3 wt.%.

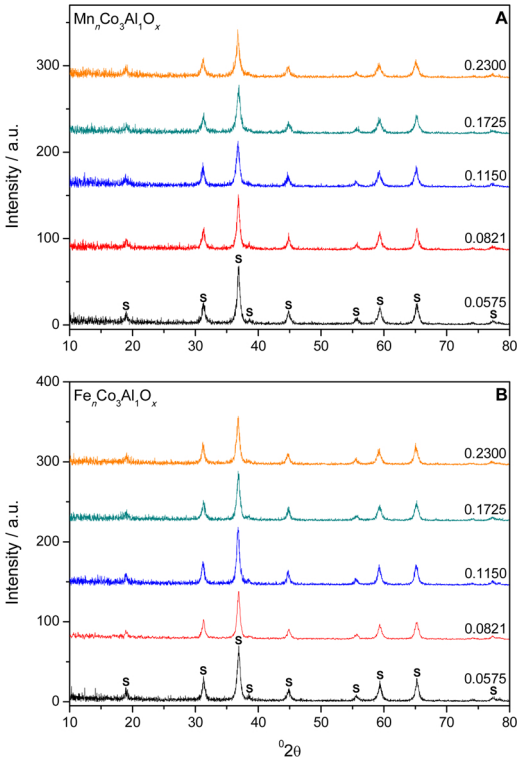

Fig. 3. X-ray diffraction patterns of $Mn(Fe)_nCo_3Al_1O_x$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%) mixed metal oxides; S – $Co_3O_4/CoAl_2O_4/Co_2AlO_4$.

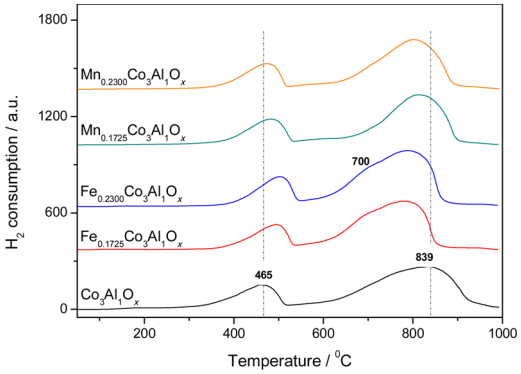

Fig. 4. H_2-TPR profiles of selected $Co_3Al_1O_x$ and $Mn(Fe)_nCo_3Al_1O_x$ (n = 0.1725, 0.2300, mol.%) mixed metal oxides; experimental conditions: mass of catalysts = 30 mg, [H_2] = 5.0 vol.%, [Ar] = 95.0 vol.%, flow rate = 25 $cm^3\,min^{-1}$, linear heating of 5 K min^{-1}.

Fig. 4 presents the H_2-TPR profiles for $Co_3Al_1O_x$ and selected $Mn(Fe)_nCo_3Al_1O_x$ (n = 0.1725, 0.2300, mol.%) mixed metal oxides. The H_2-TPR profile for Co_3Al material revealed the presence of two main reduction peaks, with maxima centered at around 465 and 839 °C. The peak at lower temperature appeared due to the complete reduction of Co_3O_4 to metallic cobalt [24–26] while the high temperature reduction peak was related to the reduction of cobalt in $Co_2AlO_4/CoAl_2O_4$ [27]. $Mn(Fe)_nCo_3AlO_x$ (n = 0.1725, 0.2300, mol.%) revealed similar H_2-TPR profiles to $Co_3Al_1O_x$. However, the modification of Co_3Al with Mn or Fe influenced its redox properties, i.e. the position of the first reduction peaks shifted to higher temperatures for Mn- or Fe-doped materials than for $Co_3Al_1O_x$, while the position of the second peak shifted to lower temperatures, indicating depressed reducibility of Co_3O_4 and improved reducibility of cobalt in Co_2AlO_4 and $CoAl_2O_4$. Such an effect was more

Table 3
Amount of H_2 consumed during H_2-TPR measurements (H_2 uptake), the peaks positions, their binding energy, peak area, full width at half maximum (FWHM) and $O_\alpha/(O_\beta + O_\gamma)$ molar ratio of mixed metal oxides.

Mixed metal oxides	H_2 uptake[a]/mmol g^{-1}	A^b/A^c/a.u.	Position Co $2p_{3/2}$ *O 1 s ■Mn $2p_{3/2}$ □Fe $2p_{3/2}$	FWHM /eV	Area /a.u.	$O_\alpha/(O_\beta + O_\gamma)$[d]
$Co_3Al_1O_x$	13.16	0.36	780.35	4.09	11998	
	3.47[b]		786.26	7.90	4073	
	9.69[c]		802.84	6.75	2239	
			*527.07	1.72	462	
			*528.77	1.92	2066	0.23
			*530.38	2.08	6369	
			*531.91	2.10	2697	
$Mn_{0.1725}Co_3Al_1O_x$	12.13	0.35	781.63	3.79	8333	
	3.14[b]		785.80	8.90	2826	
	8.99[c]		804.53	8.64	1134	
			*528.51	1.43	239	
			*530.07	2.09	2126	0.21
			*531.72	2.25	7926	
			*533.41	1.95	2106	
			■643.03	4.00	1080	
$Fe_{0.1725}Co_3Al_1O_x$	12.63	0.28	779.63	3.94	7137	
	2.75[b]		784.18	8.19	2085	
	9.88[c]		802.17	8.64	1244	
			*526.58	1.63	324	
			*528.37	2.20	2077	0.32
			*529.81	2.04	4523	
			*531.28	2.06	1933	
			□710.44	5.20	956	

[a] Calculated by equation: Y = 9E-09X + 2E-07, R^2 = 0.9996, and X, Y referred to the area of each reduction peak and the H_2 consumption, respectively.
[b] In the region.50–530 °C.
[c] In the region 530–1000 °C.
[d] Estimated from the integrated area of the respective XPS peaks.

visible for $FeCoAlO_x$. Additionally, for the Fe-containing samples a broad shoulder appeared at about 700 °C that could be ascribed either to a partial reduction of cobalt in Co_2AlO_4 and $CoAl_2O_4$ or to reduction of iron oxide species [4,5]. Taking into account, the lower loading of Mn or Fe introduced into $Co_3Al_1O_x$ in comparison to the content of cobalt and aluminum, the first assumption seems more likely. Thus, also reduction of manganese oxide species was not distinguished. Nevertheless, the up-shifting of H_2-TPR peak of Co_3O_4 suggested that Mn and Fe have to be incorporated within the spinel structure.

Table 3 summarizes H_2-TPR data of the studied materials. The H_2 uptake varied in the range of 2.75–3.47 mmol g^{-1} in the temperature range of 150–530 °C (where N_2O decomposition proceeded). Furthermore, analysis of reduction peak areas (A^b/A^c, estimated from the integrated areas of the respective H_2-TPR peaks) revealed a comparable ratio (0.28 to 0.36) across the samples. Due to different oxidation states of metal oxide species in spinel forms, the calculations of the H_2 uptake based on materials composition are at best speculative. Fig. 5 shows the Co 2p, O 1 s, Mn 2p and Fe 2p XPS spectra of $Co_3Al_1O_x$ and Mn $(Fe)_{0.1725}Co_3Al_1O_x$, while Table 3 summarizes the peaks positions, their binding energy, peak area, full width at half maximum (FWHM) and $O_\alpha/(O_\beta + O_\gamma)$ molar ratio. The Co 2p XPS spectra exhibited two main peaks characterized by binding energy in the ranges of 781.6–779.6 and 796.9–795.0 eV corresponding to the Co$2p_{3/2}$ and $2p_{1/2}$ spin-orbit peaks respectively [28]. Thus, since the spin-orbit values for the tested materials have varied in the range of 15.3–15.4 eV, we concluded that mainly Co_3O_4 (spin-orbit value of 15.2 eV) together with $CoAl_2O_4$ (as minor compound; spin-orbit value of 15.9 eV) was present on the catalyst surface [28–30]. Considering that Mn or Fe are present only in small amounts, determination of their chemical state in the measured $Mn(Fe)_{0.1725}Co_3Al_1O_x$ based on the position of the binding energy is again largely speculative. Furthermore, Mn or Fe may be present in several chemical states with the overlapping spectra, which are close in energy [11,31]. The O 1 s spectra were deconvoluted to lattice oxygen – O_α, surface adsorbed oxygen, OH groups and oxygen vacancies – O_β and adsorbed molecular water – O_γ [32]. Additional low peaks at about 527–528 eV appeared possibly due to the differential charging of the materials [33]. The molar ratio of $O_\alpha/(O_\beta + O_\gamma)$ varied in the range of 0.21–0.32.

Fig. 6 shows the XANES spectra of $Mn(Fe)_{0.1725}Co_3Al_1O_x$ mixed metal oxides. In comparison to the Co_3O_4 reference spectrum (Co K-edge), the spectrum of $Mn_{0.1725}Co_3Al_1O_x$ at room temperature showed a more intense pre-edge peak which could be rationalized as being caused by a greater proportion of Co ions with a non-centrosymmetric geometry in this sample. Furthermore, an adsorption edge at lower energies – 7717.63 eV for Co_3O_4 and 7717.100 eV for $Mn_{0.1725}Co_3Al_1O_x$ at room temperature, indicated a lower overall Co oxidation state (Fig. 6A). This suggested the presence of a $CoAl_2O_4$ type spinel where the substitution of Co^{3+} by Al^{3+} in the octahedral position leads to a higher contribution of Co^{2+} Td. Indeed, it has previously been shown that $CoAl_2O_4$ type spinel phase can form at temperatures as low as 390 °C [34]. The Mn K-edge spectra acquired at room temperature (Fig. 6B) closely resembled that of a Mn_3O_4 spinel reported previously [35]. To date no XAFS data exists concerning mixed Mn and Co spinels although a detailed XRD/vibrational spectroscopic study of Co/Mn substitution suggests that such phases can readily be formed and therefore a mixed $Mn_xCo_yO_4$ and/or $Mn_xCo_yAl_zO_4$ could be present in the $Mn_{0.1725}Co_3Al_1O_x$ sample [36]. For $Fe_{0.1725}Co_3Al_1O_x$ mixed metal oxides measured at room temperature, Co K-edge XANES revealed comparable Co speciation to the Mn-containing sample (Fig. 6E). Nevertheless, the Fe XANES spectrum closely resembled that of α-Fe_2O_3 (Fig. 6F), suggesting that unlike Mn, Fe did not incorporate so readily into the Co_3O_4 structure. In agreement, the shift to higher temperatures of Co_3O_4 reduction peak in the H_2-TPR profile suggested that small amounts of iron must have incorporated into the spinel structure thereby affecting its redox properties.

Changes occurring in $Mn_{0.1725}Co_3Al_1O_x$ mixed metal oxides, during thermal treatment (up to 600 °C) in the presence of He and N_2O/He,

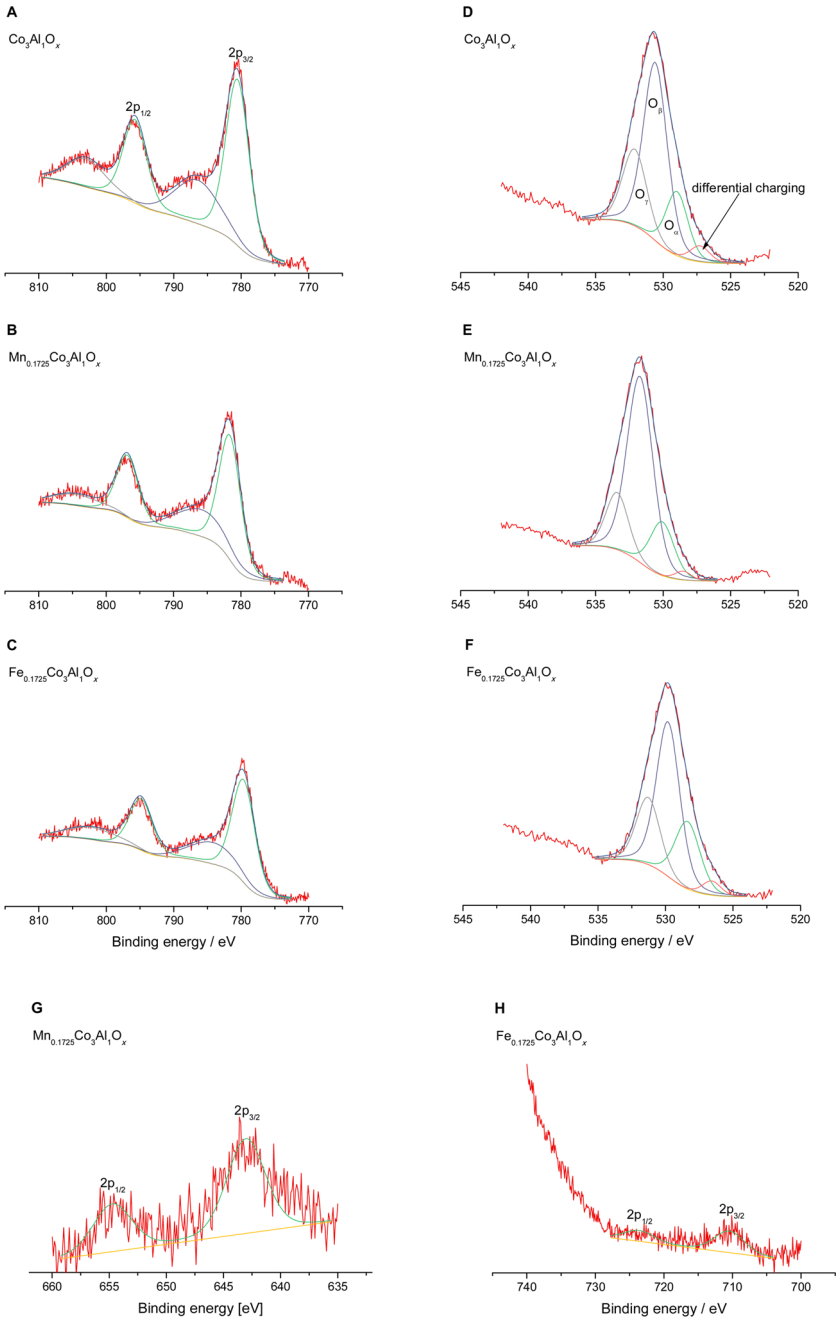

Fig. 5. XPS spectra of $Co_3Al_1O_x$ and $Mn(Fe)_{0.1725}Co_3Al_1O_x$ mixed metal oxides; Co 2p (A–C), O 1 s (D–F), Mn 2p (G) and Fe 2p (H).

were followed by studying the Co and Mn K-edge XANES spectra. A shift in the Co absorption edge to lower energies as well as a decrease in the pre-edge intensity were observed upon He treatment at 600 °C, which is indicative of a decrease in the nominal valence of Co in the material (Fig. 6A). The spectra resembled that of the CoO reference constituted by Co^{2+} in an octahedral environment. However, the higher pre-edge intensity of the sample when compared to CoO/Co_3O_4 suggested some Co^{2+} was still present in a tetrahedral environment. Considering the H_2-TPR results pertaining to the reducibility of both cobalt oxide species present in the catalyst, it seems that $Mn_xCo_yO_4$ is reduced to (Mn)CoO while $CoAl_2O_4$, with Co^{2+} in a tetrahedral environment, remained unchanged. EXAFS *k*-plots for Co and Mn in $Mn_{0.1725}Co_3Al_1O_x$ before and after reduction are shown in Fig. 1S in the Supplementary information. At room temperature the Mn and Co fine structure resembled closely the Co_3O_4 reference while in the reduced sample the fine structure is similar to CoO. This further confirms the presence of the initial spinel environment for both Mn and Co and that in both cases this evolves into the rock salt $M^{2+}O$ phase. Similar to Co, Mn also undergoes reduction upon activation in He at 600 °C; the reduced spectra resembling features of MnO [35]. Finally, in the presence of N_2O/He, both Co and Mn oxide species reoxidized to their initial state. Fig. 6C and D show the temperature dependence of this reoxidation process; the spectral changes were observed at 300–450 °C temperature range which coincided with the temperature needed to obtain full N_2O conversion. MnO appeared easier to reoxidize than CoO since the spectral changes in Mn K-edge XANES commenced at 300 °C while changes in Co K-edge occurred at 350 °C.

Furthermore, the changes in the oxidation state of Co at different reaction stages in $Mn_{0.1725}Co_3Al_1O_x$ were studied by the investigation of the position of the absorption edge (defined as the first maximum of the derivative plot beyond the pre-edge peak). Table 4 presents the Co K-edge absorption positions relative to Co foil ($\Delta E = E_{sample} - E_{foil}$) of

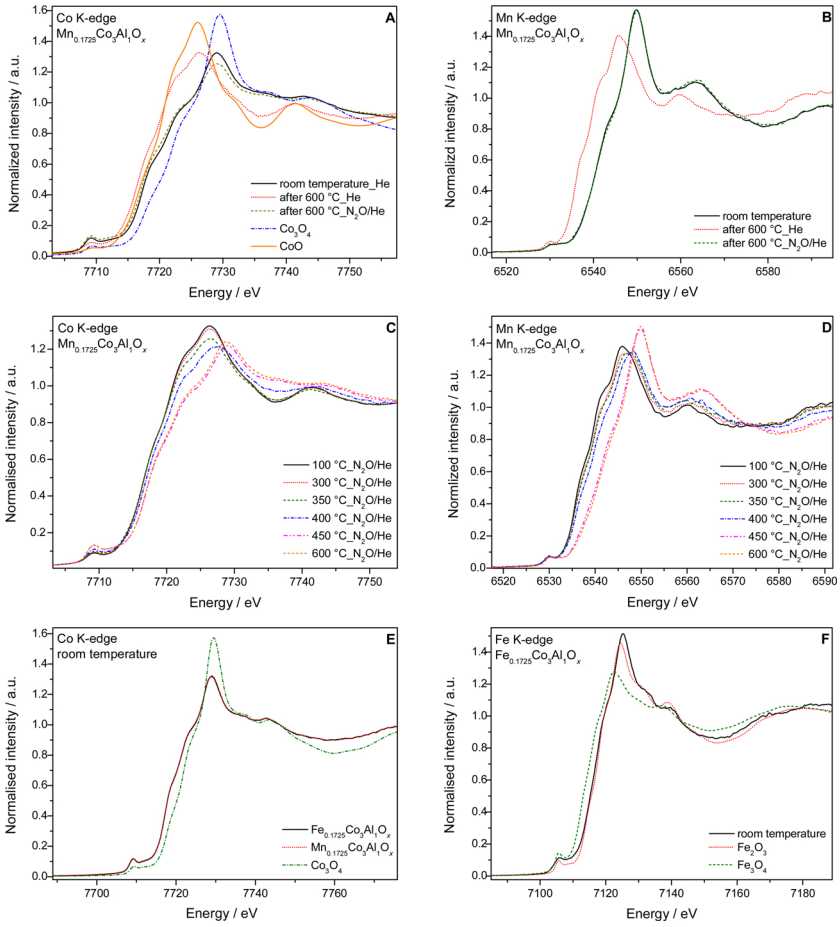

Fig. 6. In situ XANES spectra of A) Co K-edge for $Mn_{0.1725}Co_3Al_1O_x$ at different reaction stages and Co references; B) Mn K-edge for $Mn_{0.1725}Co_3Al_1O_x$ sample acquired at different stages of reaction; C) Co K-edge during the temperature ramp under N_2O; D) Mn K-edge during the temperature ram under N_2O; E) Co K-edge for $Mn_{0.1725}Co_3Al_1O_x$, $Fe_{0.1725}Co_3Al_1O_x$ and Co_3O_4 reference at room temperature; and F) Fe K-edge for $Fe_{0.1725}Co_3Al_1O_x$ and references.

Table 4
Co K-edge energy position relative to Co foil (E_0) for $Mn_{0.1725}Co_3Al_1O_x$ at room temperature, after reduction under He and after reoxidation under N_2O/He at 600 °C as well as references at room temperature.

Mixed metal oxides	ΔE/eV	References	ΔE/eV
$Mn_{0.1725}Co_3Al_1O_x$		room temperature	
room temperature	8.1	CoO	7.4
after He 600 °C	7.4	Co_3O_4	8.5
after N_2O/He 600 °C	8.1		

Table 5
Coordination number (CN), bond distances between adsorbed and backscatter atoms (R), inner potential correction to account for the difference in the inner potential between the sample and the reference compound (E), Debye-Waller factor ($2\sigma^2$), and residual factor (Rf) of $Mn_{0.1725}Co_3Al_1O_x$ mixed metal oxides.

Mixed metal oxides	Shell Co-O	CN	R/nm	ΔE_0/eV	$10^2*\sigma^2$/nm	R_f/%
$Fe_{0.1725}Co_3Al_1O_x$						
room temperature He[a]		4.0	0.191	3.75	0.049	2.63
$Mn_{0.1725}Co_3Al_1O_x$						
room temperature He[a]		4.0	0.191	3.05	0.041	2.65
after He 600 °C[b]		6.0	0.206	−0.04	0.134	4.53
after N_2O/He 600 °C[a]		4.0	0.191	3.28	0.067	3.79

[a] fitting of the spectra collected at room temperature.
[b] fitting of the spectra collected at 100 °C.

$Mn_{0.1725}Co_3Al_1O_x$ at different stages of the experiment as well as the ΔE of Co_3O_4 and CoO references. Again, the ΔE of the sample after treatment with He at 600 °C was comparable to CoO. While the reoxidation, under N_2O/He conditions, leads to the recovery of its initial oxidation state. Table 5 lists the results of the curve-fitting analysis for the first coordination shell. First shell quick fit analysis of the EXAFS was carried out to gain insight into the average Co—O distances and coordination numbers. The fitting was performed for the Co K-edge spectra of $Mn_{0.1725}Co_3Al_1O_x$ collected at room temperature prior to the activation, for the spectra collected after the activation in He (once cooled down at 100 °C under He) and for the spectra collected at room temperature after the N_2O/He treatment at 600 °C. For comparison, Co K-edge spectra of $Fe_{0.1725}Co_3Al_1O_x$ at room temperature (prior thermal treatments) was also fitted. The results revealed higher Co—O bond distances of 206 nm for $Mn_{0.1725}Co_3Al_1O_x$ after activation with He at 600 °C. Due to the presence of mixed sites and slightly higher temperature in the spectra acquisition of the preactivated sample, the DWF and CN values become meaningless; nonetheless, the bond length, being less affected by such factors, suggests the presence of a CoO type structure with Co^{2+} Oh. Otherwise, $Mn_{0.1725}Co_3Al_1O_x$ at room temperature or in the presence of N_2O/He at 600 °C showed a shorter Co—O of 0.191 nm, corresponding mainly to the presence of a spinel phase. As expected from XANES, the Co—O shell fitting gave very similar results for $Mn_{0.1725}Co_3Al_1O_x$ and $Fe_{0.1725}Co_3Al_1O_x$ at room temperature.

Fig. 7 presents the results of catalytic tests performed over Mn(Fe)$_n$$Co_3Al_1O_x$ (n = 0.0575, 0.0821, 0.1150, 0.1725, 0.2300, mol.%), while Table 2 lists temperatures necessary to obtain 50% N_2O conversion (T_{50}). The particle size of 0.250–0.500 mm of our samples used for the catalytic measurements was in the same scale order than the particle size of the samples of the study reported by Klyushina et al. [23], who reported the absence of internal and external diffusion limitations. Moreover, the reactor diameter and the catalyst bed length criteria requirement were checked. D(reactor diameter/dp(particle diameter ≈ 16 was above) and L (catalyst bed length)/dp was superior to 50. Therefore, we can certify that the catalytic reactions were realized in kinetic regime. The N_2O conversion

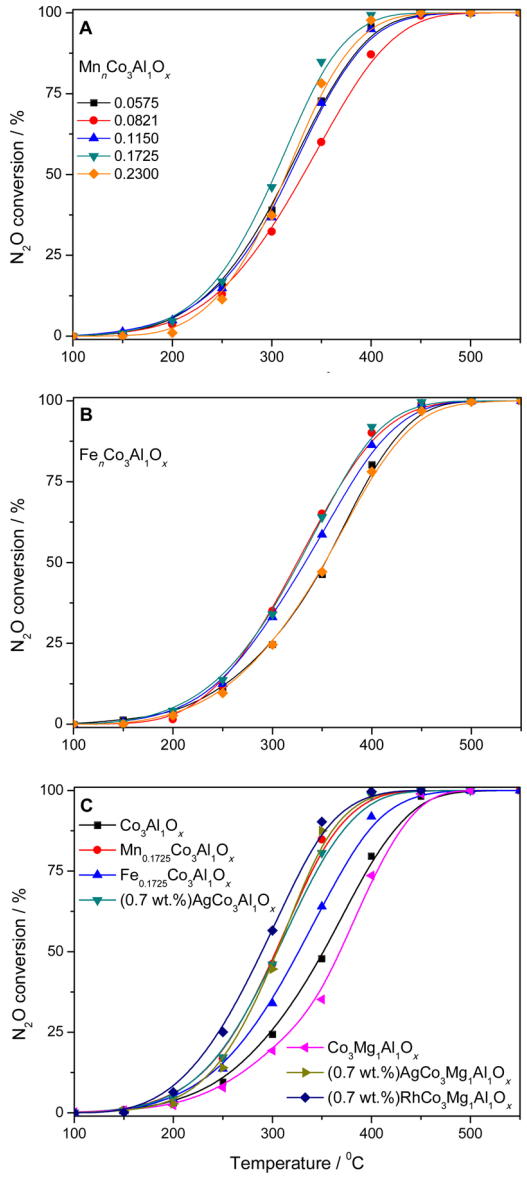

Fig. 7. Results of catalytic tests performed over $Co_3Al_1O_x$, $Mn(Fe)_nCo_3Al_1O_x$ (n = 0, 0.0575, 0.0821, 0.1150, 0.1725, 0.2300) and (0.7 wt.%)Ag(Rh)$Co_3(Mg_1)Al_1O_x$ mixed metal oxides; reaction conditions: mass of catalysts = 350 mg, [N_2O] = 0.1 vol.%, N_2 balance, total flow rate = 100 $cm^3\,min^{-1}$, WHSV of 17 L $(h\ g)^{-1}$.

from the reaction mixture started at about 150–200 °C, while full conversion was reached at about 450–500 °C for all tested materials. $Co_3Al_1O_x$ reached T_{50} at about 352 °C with the full conversion at 500 °C. Incorporation of Mn or Fe into $Co_3Al_1O_x$ structure improved the catalytic activity of mixed metal oxides. An exception was $Fe_{0.2300}Co_3Al_1O_x$, which showed catalytic activity similar to $Co_3Al_1O_x$. The reproducibility of our catalytic tests was confirmed by repeated measurements. The activity differentiated among tested materials however showed no clear trend and was neither related to the Mn or Fe nor Na (up to 2.3 wt.%) content. Alkali metals (e.g. Na, K, Li) can act as basic centres and influence catalytic activity. For example, Obalová et al. [12] pointed out that 1.15 wt.% of Na introduced by impregnation already slightly enhanced activity of Co_4MnAlO_x. However, materials with Na loaded by impregnation were reported to stronger facilitate N_2O decomposition than when Na was present after preparation [37,38]. The optimum amount of deposited Na varied also depending on the applied mixed metal oxides: 0.75 wt.% for $Co_{2.5}Rh_{0.05}Al_1O_x$ [38], 1.5 wt.% for $Co_3Al_1O_x$ [39] or 1.4 wt.% for $Co_4Mn_1Al_1O_x$ [40]. Farris et al. [41] found out that an optimum Na residual content in the range of 3.0–6.0 wt.% in $CoAlO_x$ was supposed to promote the decomposition of N_2O facilitating over 80% conversion at 475 °C. Doping with 1.0–2.0 wt.% of Na resulted in comparable results. In our case the amount of residual Na varied significantly from 0.7 up to 2.3 wt.% among samples despite application of the same material preparation procedure (including washing step). At this stage, it is not possible to precisely justify the influence of residual Na on materials activity in deN_2O. Certainly, further research should be carried out in order to clarify these remarkable observations over investigated (Mn,Fe)$CoAlO_x$ mixed metal oxides, considering also the synergistic effect of Mn(Fe) and residual Na on the catalytic activity.

The highest activity among tested materials reached $Mn_{0.1725}Co_3Al_1O_x$ with T_{50} at 305 °C and full conversion at 400 °C. Furthermore, $Mn_{0.1725}Co_3Al_1O_x$ possessed comparable activity to the Ag-doped catalysts – (0.7 wt.%)$AgCo_3(Mg_1)Al_1O_x$, and only slightly lower activity than the (0.7 wt.%)$RhCo_3Mg_1Al_1O_x$, reported as one of the most active and stable hydrotalcite derived mixed metal oxides in the N_2O decomposition with excellent activity and stability performance [7,42]. Catalytic tests were carried out under the same reaction conditions (Fig. 7C). Details regarding preparation, characterization and discussion of activity of both Ag- and Rh-containing mixed metal oxides were reported in our previous studies [43].

$Co_3Al_1O_x$ and $Mn(Fe)_{0.1725}Co_3Al_1O_x$ were also tested in the presence of NO and O_2 (350 mg of catalyst, 100 $cm^3\,min^{-1}$ total flow). $Mn_{0.1725}Co_3Al_1O_x$ presented T_{50} of 376 °C, thus temperature of about 70 °C higher than for tests without NO and O_2. Slightly lower activity above 350 °C was obtained over $Fe_{0.1725}Co_3Al_1O_x$ with T_{50} at 380 °C. Furthermore, for practical applications, $Co_3Al_1O_x$ and $Mn(Fe)_{0.1725}Co_3Al_1O_x$ were tested in the presence of H_2O (70 mg of catalyst, 75 $cm^3\,min^{-1}$), as displayed on Fig. 2SA. $Mn_{0.1725}Co_3Al_1O_x$ showed the highest resistance to water vapour with T_{50} of 549 °C. Other materials presented significantly lower resistance to water vapour. Fig. 2SB presents the contribution of NO formation over $Co_3Al_1O_x$ and $Mn(Fe)_{0.1725}Co_3Al_1O_x$. The highest amount of such by-product in N_2O decomposition appeared over $Fe_{0.1725}Co_3Al_1O_x$. For other materials the formation of NO did not exceed 15 ppm in the studied temperature range of 200–550 °C. Notably, for catalytic tests carried out in the presence of water vapour NO formation decreased. In Fig. 3S, time-on-stream tests were conducted to evaluate the stability of $Co_3Al_1O_x$ and $Mn(Fe)_{0.1725}Co_3Al_1O_x$ at 450 °C. All materials showed stable conversion during the first 85 min in the N_2O/N_2 feed. Subsequently, after introduction of water vapour into the feed, the conversion of all materials significantly dropped reaching a stable level below 20%. However, switching from wet to a dry reaction mixture resulted in an increase in catalyst conversion back to the initial dry level. Thus, the introduction of H_2O into the feed did not result in an irreversible deactivation of the catalysts.

Obalová et al. [11] reported that the high activity of $Co_4Mn_1Al_1O_x$ hydrotalcite derived mixed metal oxides appeared due to an optimum content of components reducible in the temperatures of the maximum conversion of N_2O (between 350–450 °C). Analysis of our reduction peak areas showed similar ratio (0.28 to 0.36) across the samples. Crystal sizes were calculated from (3 1 1) brag reflection in the XRD patterns using the Scherrer equation; comparable results of 27, 26 and 30 nm for $Co_3Al_1O_x$, $Mn_{0.1725}Co_3Al_1O_x$ and $Fe_{0.1725}Co_3Al_1O_x$, respectively, discard size effects in the catalytic activity and selectivity. In addition, no significant effect of textural properties on the catalytic results was found (S_{BET} of 82, 76, 54 $m^2\,g^{-1}$ for $Co_3Al_1O_x$, $Mn_{0.1725}Co_3Al_1O_x$ and $Fe_{0.1725}Co_3Al_1O_x$, respectively). Although, the strength of lattice oxygen-metal bonds was reported to determine the catalysts activity in deN_2O [44], we did not observe clear correlation between $O_\alpha/(O_\beta + O_\gamma)$ molar ratio and catalytic activity/selectivity of mixed metal oxides. Mn in $Mn_{0.1725}Co_3Al_1O_x$ appeared incorporated within spinel structure; MnO and CoO phases present after activation reoxidize under N_2O/He feed. Indeed this observation of Mn being

easier to oxidise back to 3+ than Co, yet harder to reduce to 2+ is completely consistent with the respective redox potentials of the two elements [45]. On that basis Fe in $Fe_{0.1725}Co_3Al_1O_x$ could play a similar role as Mn. Nevertheless, as most of the iron was not incorporated to the spinel but appeared as separate Fe_2O_3 phase, its effect on catalytic activity was less pronounced than for Mn in the $Mn_{0.1725}Co_3Al_1O_x$ sample. Accordingly, decomposition of N_2O over the tested mixed metal oxides followed the cationic redox mechanism [42–44], consisting of N_2O activation by electron transfer from metal sites and diffusive recombination of the surface oxygen intermediates into oxygen, concerted with the back electron transfer that restores the oxidation state of the active sites. The regeneration of the active sites through oxygen desorption is considered as the rate-determining step. In this context, Co oxidizes when N_2O is adsorbed and then Co is again reduced when O_2 is released. Thus, during reaction under N_2O/He conditions, Co is continuously oxidizing and reducing. The doping, in particular Mn, may generate new redox sites on the surface or may enhance the oxygen desorption from cobalt sites. Taking into account the very weak amount of manganese added and the fact that manganese appeared incorporated within the structure, the latter assumption seems more likely. Further studies will certainly aim for a deeper understanding of the individual role of the catalyst components in deN_2O.

4. Conclusion

$Mn(Fe)_nCo_3Al_1O_x$ (n = 0.0575, 0.0821, 0.115, 0.1725 and 0.2300, mol.%) hydrotalcite derived mixed metal oxides were synthesized by coprecipitation and subsequent calcination. The catalytic activity of $Co_3Al_1O_x$ mixed metal oxides was improved in deN_2O by incorporation of an appropriate amount of Mn or Fe. $Mn_{0.1725}Co_3A_1O_x$ reached the highest activity with T_{50} of about 305 and 376 °C under N_2O/N_2 and N_2O,NO,O_2/N_2 feed, respectively. The trend for catalytic conversion was $Mn_{0.1725}Co_3A_1O_x > Fe_{0.1725}Co_3A_1O_x > Co_3A_1O_x$. Detailed evaluation of the active species was realized by an in situ XAFS study. Correlation of the catalytic data with the XAS results suggested that doping Co_yO_4 spinel by Mn(Fe)lead to a facilitated desorption of oxygen. The presence of Mn in the spinel structure seemed to provide active surface Co sites that release oxygen more easily. The lower activity of the $Fe_{0.1725}Co_3Al_1O_x$ mixed metal oxides was attributed to the fact that Fe did not incorporate so readily into the cobalt spinel structure forming less active iron oxide clusters instead.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.10.010.

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